



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁶ :

C25B 9/00, 1/26, C01B 11/02

A1

(11) International Publication Number:

WO 98/32900

(43) International Publication Date:

30 July 1998 (30.07.98)

(21) International Application Number: PCT/NL98/00047

(22) International Filing Date: 23 January 1998 (23.01.98)

(30) Priority Data:

1005081

24 January 1997 (24.01.97)

NL

(71) Applicant (for all designated States except US): ZILVOLD-TIELEMAN HYDROTECHNIEK B.V. [NL/NL]; Broekhuizerweg 4, NL-6983 BM Doesburg (NL).

(72) Inventor; and

(75) Inventor/Applicant (for US only): ZILVOLD, Hendrik, Martin [NL/NL]; Eertbornweg 6, NL-8084 EN 't Harde (NL).

(74) Agent: VAN KAN, J., J., H.; Algemeen Octrooibureau, World Trade Center, Past. Petersstraat 160, NL-5612 LV Eindhoven (NL).

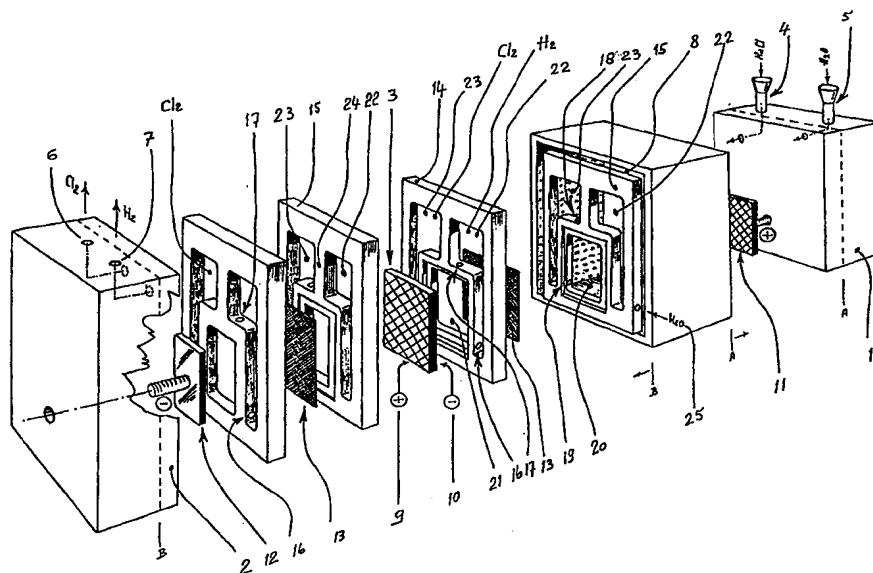
(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

With international search report.

In English translation (filed in Dutch).

(54) Title: PROCESS AND APPARATUS FOR THE ELECTROLYTIC PRODUCTION OF CHLORINE AND USE THEREOF



(57) Abstract

A device for carrying out the electrolysis of a chloride, wherein the cathode space (21) is in direct communication with the catholyte space (22), which catholyte space also functions as an outlet for hydrogen gas, and wherein the anode space (20) is in direct communication with the anolyte space (23) which anolyte space functions as an outlet for chlorine gas, whereby there is no communication between the catholyte space and the anolyte space. The invention furthermore relates to a cell element to be used therein, to a method for carrying out an electrolytic process in such a device, and to the use of the chlorine gas thus obtained for preparing chlorine dioxide, and also to a reactor and an installation suitable for that purpose.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

PROCESS AND APPARATUS FOR THE ELECTROLYTIC PRODUCTION OF CHLORINE AND USE THERE OF

5

10

15

20

The present invention relates to a device for carrying out the electrolysis of a chloride, wherein several electrolytic cells are connected electrically in series, which cells consist of a cell element, a bipolar electrode and a diaphragm or a semi-permeable membrane, wherein said cells are surrounded by an encasing comprising two end plates, and wherein a liquid jacket is present between the encasing and the outside of the cell frames, which jacket is provided with an inlet and an outlet for said liquid. The present invention furthermore relates to a cell element for use in such a device for carrying out an electrolytic process and to a method for carrying out an electrolytic process in such an electrolysis device. In addition to that the present invention relates to the use of the chlorine gas obtained in accordance with the present invention as well as to a reactor therefore and to an installation for preparing chlorine dioxide.

25

30

35

Such a method for carrying out the electrolysis of a chloride is known from European patent No. 0 427 340. According to said European patent a liquid jacket is provided within the encasing of the series-connected electrolytic cells, round the system of the cell frames comprising bipolar electrodes and separators or degassing tubes, which liquid is preferably water. Such a liquid jacket functions to allow possible leakage from the electrolytic cells, because the liquid that may leak out will be caught in the water jacket, which is refreshed periodically or continuously, and which may subsequently be used specifically as a catholyte. A small amount of in-leakage is acceptable thereby. In addition to that a separation of an electrolyte and the gas that has developed takes place in the degassing tubes, so that hydrogen and chlorine gas can readily be recovered from said degassing tubes. A problem with such electrolytic apparatus, which comprises several series-connected bipolar electrodes, is that a great deal of attention must be paid to the proper sealing of the cells, so that no leakage of the electrolyte from the electrolytic cell will occur. Although it is not

necessary with the construction described in the aforesaid European patent to pay special attention to the packing material and to the stresses which are necessary thereby, which stresses are exerted on the cell frames in which the bipolar electrodes are placed, there is still a small amount of leakage at the degassing tubes in practice. In addition to being toxic, the chemical substances produced during the electrolysis are also highly corrosive, so that the materials to be used need to meet certain requirements. Moreover, the use of such degassing tubes requires precise fitting in the end plates.

The object of the invention is therefore to provide a device for carrying out an electrolytic process, wherein the occurrence of leakage of the electrolyte from the electrolytic cell is prevented. In addition to that it is desirable to develop an electrolysis device which does not require the use of separate degassing tubes.

According to the present invention the device referred to in the introduction is characterized in that the cathode space is in direct communication with the catholyte space, which catholyte space also functions as an outlet for hydrogen gas, and that the anode space is in direct communication with the anolyte space, which anolyte space functions as an outlet for chlorine gas, whereby there is no communication between the catholyte space and the anolyte space.

Although German Offenlegungsschrift No. 36 03 254 discloses a cell frame which is composed of a cathode gas part and an anode gas part, which parts are in communication with the electrolytic cell part via a communication opening, there is still a risk of leakage with such an electrolytic cell unit. The leakage problems are caused by the fact that the cell frames are connected into a block by using draw rods. The individual cell frames are therefore provided with a sealing material, preferably polyfluoroethylene. This is a construction which is known per se, and which is frequently used for filter pressing. With the lapse of time the poor sealing along the circumference of the individual cell frames will lead to loss of process liquids and gases. In addition, the device is only suitable for the electrolysis of water, wherein oxygen and hydrogen are produced.

The present invention, on the other hand, is suitable for carrying out the electrolysis of a chloride compound, wherein the corrosive chlorine gas and the explosive hydrogen gas are formed. The

special medium to be subjected to electrolysis makes it necessary to pay a great deal of attention to keeping the process liquids and gas within the present device. In particular the leakage into the environment of the chlorine gas prepared by electrolysis must absolutely be prevented for environmental and safety reasons. The present invention has solved the problem of leakage of process liquids and gases in a way which essentially differs from the method disclosed by the aforesaid German Offenlegungsschrift, namely by providing a liquid jacket between the encasing and the outside of the cell frames. Thus the end plates can provide a mechanical fixation without using draw rods, which cause leakage, which makes the present construction essentially different from the construction known from German Offenlegungsschrift No. 36 03 254.

The device for carrying out such an electrolytic process is preferably built up of series-connected electrolytic cells in such a manner that the cathode space and the anode space are arranged in alternate relationship, which is necessary due to the fact that a bipolar electrode is used.

The cell element which is used in the electrolytic cell is characterized in that the connection between the cathode space and the catholyte space comprises two openings, one opening of which is present in the underside for supplying catholyte and one opening is present in the upper side for discharging hydrogen gas-containing catholyte. Such a construction ensures that the hydrogen gas which is produced at the cathode during the electrolysis can exit the cathode space via the opening present on the upper side. The hydrogen gas which is thus transported from the cathode space to the catholyte space, which hydrogen gas accumulates in the space present above the surface of the catholyte liquid, ensures that "fresh" catholyte is drawn into the cathode space via an opening present in the underside. In the cathode space the fresh catholyte material is subsequently converted into hydrogen gas, which gas exits the cathode space via the opening present in the upper side. The use of two openings ensures that there will be a continuous supply of fresh starting material and a continuous discharge of reaction products.

The other cell element which is used in the device for carrying out the electrolysis as described above is characterized in that the connection between the anode space and the anolyte space comprises two openings, one opening of which is present in the underside for

supplying anolyte, and one opening is present in the upper side for discharging chlorine gas-containing anolyte. In the anode space the chlorine gas thus formed can exit the anode space via the opening present in the upper side. The chlorine gas thus transported from the anode space to the anolyte space will accumulate above the surface of the anolyte liquid in the anolyte space. The opening present in the underside ensures that "fresh" anolyte is transported from the anolyte space to the anode space, thus ensuring that there will be a continuous supply of fresh starting material via the opening in the underside and a continuous discharge of reaction products via the opening on the upper side. Such a process is also referred to as a bubble pump.

Such cell elements are preferably configured in such a manner that the volume of the space for discharging the gas being produced is larger than the volume of the space adjacent to the space that houses the bipolar electrode. Such geometry makes it possible to use a small amount of liquid in the electrolytic cell in order to keep the two openings for supplying starting material and discharging reaction products below the liquid level, as described before. It should be apparent that the transport process thus described (the "bubble pump"), which takes place in the anolyte space as well as in the catholyte space, can only be carried out if both openings are located below the liquid level.

It is furthermore preferred to build up the cell element as one unit, so that dimensional stability is ensured. This will prevent possible stresses from leading to leakage, which is one of the objectives of the present invention. In addition, such cell elements can be produced in a simple manner with great dimensional precision. It is in particular preferred for the cell element to have a rectangular geometry, whereby the part that constitutes the anolyte space and the part that constitutes the catholyte space have a P-shaped structure, wherein the P-shaped structures are positioned within the cell element, and wherein said structures are separated from each other by an intermediate member and by the space into which the bipolar electrode is to be placed. Thus the desired bell pump function can be effected by using a small amount of liquid in the anolyte space and in the catholyte space.

The device according to the present invention is furthermore characterized in that the electrolytic cells are pressed together under a prestressing force, whereby the outer shell is indirectly

connected to the electrically series-connected electrolytic cells in a fluid-tight manner by being glued, bolted or welded thereto. By first pressing together the electrolytic cells and then welding or glueing the enveloping or surrounding water jacket to the two end plates under a pre-stressing force, a proper water-tightness of the jacket is ensured. Moreover, a proper sealing action between the individual cell elements is ensured with such a construction.

The cell element which is used in the device for carrying out an electrolytic process according to the present invention is furthermore provided with a recess, into which the bipolar electrode can be placed, which recess is provided with ridges all round. The use of ridges ensures that the bipolar electrode is properly sealed in the recess of the cell element, thus preventing leakage of the liquid that is present in the cathode space into the anode space, and vice versa. Preferably such ridges are also present on the cell element, in order to ensure that the diaphragm is properly fixed and sealed in the cell element.

There is a great demand for the chlorine gas which is produced during electrolysis, in particular for purifying swimming water in swimming pools. The device according to the present invention may also be used, however, for preventing algal growth in cooling towers, for pasteurising milk or ice-cream, which may also take place by means of UV light, and generally in those places where germs and the like are to be killed.

From practice it has become apparent, however, that a faster and better oxidation and disinfection of for example water may take place if ClO_2 is added besides chlorine. A significant improvement achieved by using such a method of water treatment is the absence of the odour of the water thus treated, which people often consider objectionable. It is desirable, therefore, to provide a use for the chlorine gas developed in accordance with the present invention for the preparation of chlorine dioxide, after which chlorine dioxide can be added to water, for example.

The method for preparing chlorine dioxide by reacting chlorine gas with sodium chlorite is characterized in that the chlorine gas obtained by carrying out the above-described method is used. The formation of chlorine dioxide by using the chlorine gas obtained in accordance with the present method is not limited to sodium chlorite, but any other compound which is capable of forming chlorine dioxide by reacting

with chlorine gas will be suitable. Examples of such compounds are potassium chlorite, calcium chlorite, in particular the alkaline-earth and alkali metal compounds of chlorite.

The preparation of chlorine dioxide by reacting sodium chlorite with chlorine gas is known per se from German Auslegeschrift No. 1 173 069. Said Auslegeschrift uses a gas bottle filled with chlorine gas as the chlorine gas source, whereas the present invention is limited to the special use of chlorine gas obtained by using the method according to the present invention, that is, the carrying out of an electrolytic process in the device according to the present invention. Such a special use of chlorine gas obtained by electrolysis of a chloride compound cannot be derived from said document.

The reaction is preferably carried out at a reduced pressure, which has a favourable effect on the reaction equilibrium. In addition, the chlorine produced in the present electrolysis device can thus be simply transported to the reactor for preparing chlorine dioxide. In a preferred embodiment the chlorine gas prepared in accordance with the present method is mixed with an inert carrier gas prior to being reacted with sodium chlorite, as a result of which sufficiently high gas velocities can be achieved. In a special embodiment it is preferred to mix the inert carrier gas with the chlorine gas prepared in accordance with the present method in the anolyte space of the present device already. It is also possible, however, to mix the chlorine gas with the inert carrier gas after it has exited the present electrolysis device. It is possible to use air as the inert carrier gas, but also any other inert carrier gas, such as argon or helium, is suitable. The sodium chlorite is present in the reactor in the form of a solution, and in order to increase the contact between the chlorine gas prepared in accordance with the present method and said sodium chlorite the reactor is provided with packing material, for example Rasschig rings.

In practice it is preferred to couple the present device for carrying out the electrolytic process to the reactor for preparing chlorine dioxide, as a result of which a compact installation which is easy to handle is obtained. In addition, such an installation may be provided with a control valve, as a result of which not only chlorine dioxide, but also chlorine gas is supplied to the medium to be disinfected. Experiments have shown that the combination of chlorine gas and ClO_2 has

a favourable effect on the oxidation of for example swimming pool water.

The invention will be explained in more detail hereafter with reference to the following description, wherein reference is made to the appended drawing.

5 The figure shows a device according to the present invention, which consists of several electrolytic cells comprising bipolar electrodes, wherein the device is shown in sectional view.

 The figure is a sectional view of the device according to the present invention, which consists of an encasing comprising two
10 end plates 1 and 2 provided with a positive pole 11 (anode) and a negative pole 12 (cathode), between which several electrolytic cells are present, with each cell consisting of a bipolar electrode 3 and a diaphragm 13. Bipolar electrode 3 may be considered to be a cathode 10 and an anode 9, which are both welded to a central plate (not shown) of bipolar electrode
15 3. The electrolytic cells are provided with an inlet 4 for brine and an inlet 5 for water, whereby brine is converted into chlorine gas in the device thus shown, which chlorine gas is discharged via pipe 6. The hydrogen gas produced in the device is discharged via pipe 7. The brine enters anolyte space 23 of cell element 15. The anolyte space is filled
20 with the brine solution via the opening 19 present in the underside of cell element 15. The formation of chlorine gas takes place on the anode 11 present in the anode space, after which the chlorine gas thus formed exits anode space 20 via the opening 18 present in the upper side of cell element 15. In the anolyte space 23 the liquid level of the brine solution
25 has been selected such that opening 18 as well as opening 19 are located below the brine surface. The chlorine gas that is produced will accumulate in the anolyte space above the liquid level of the brine solution. Then a continuous supply of the starting material, brine solution, into anode space 20 will take place via the opening 19 present in the underside, and
30 chlorine gas being produced will be discharged via opening 18. Anode space 20 is separated from cathode space 21 by means of diaphragm 13. Present in cathode space 21 is the water from inlet 5. The water will be converted into hydrogen gas on cathode 10, whereby the hydrogen gas will exit cathode space 21 via the opening 17 present on the upper side of cell element 14.
35 The hydrogen that is produced accumulates in catholyte space 22 above the surface of the water present therein. A continuous supply of "fresh" water from catholyte space 22 to cathode space 21 takes place via the opening

16 present in the underside of cell element 14. The liquid level in catholyte space 22 is adjusted such that opening 17 as well as opening 16 will be located below the liquid surface. It is apparent that the hydrogen gas present in catholyte space 22 cannot come into contact with the chlorine gas present in anolyte space 23, due to the presence of intermediate member 24 in cell elements 14, 15. As can be seen in the figure, the geometry of cell element 14, 15 is such that both the catholyte space 22 and the anolyte space 23 have a P-shaped structure, whereby the P-shaped structure is determined by the space into which bipolar electrode 3 is to be placed and by intermediate member 24. From the figure it is apparent that cell elements 14, 15 are placed in alternate relationship in the electrolytic cell. The reason for this is that in cell element 14, in which openings 16 and 17 are present, the hydrogen gas is formed on cathode 12, whilst cell element 15, in which cell element chlorine gas is formed, is provided with openings 18, 19. The liquid jacket between encasing 25 and cell elements 14, 15 is indicated by reference numeral 8. Any leakage of anolyte or catholyte between the cell elements 14, 15 will be caught in water jacket 8.

The chlorine gas formed in the present electrolysis device is discharged via pipe 6. The chlorine gas 6 thus discharged may subsequently be used for preparing chlorine dioxide by reacting the chlorine gas prepared in accordance with the present method with sodium chlorite or with a similar compound, which, when reacted with chlorine gas, produces the chlorine dioxide aimed at. Preferably the chlorine gas is mixed with an inert carrier gas, in particular air, prior to being reacted with sodium chlorite. Such a reaction between sodium chlorite and chlorine gas is preferably carried out at a reduced pressure, which has an advantageous effect on the reaction equilibrium. In order to augment the contact between the liquid sodium chlorite and the gaseous chlorine gas, the reactor in which the preparation of chlorine dioxide is carried out is provided with a packing elements.

CLAIMS

1. A device for carrying out the electrolysis of a chloride, wherein several electrolytic cells are connected in series electrically, which cells consist of a cell element, a bipolar electrode and a diaphragm or a semi-permeable membrane, wherein said cells are surrounded by an encasing comprising two end plates, and wherein a liquid jacket is present between the encasing and the outside of the cell frames, which jacket is provided with an inlet and an outlet for said liquid, characterized in that the cathode space is in direct communication with the catholyte space, which catholyte space also functions as an outlet for hydrogen gas, and that the anode space is in direct communication with the anolyte space, which anolyte space functions as an outlet for chlorine gas, whereby there is no communication between the catholyte space and the anolyte space.
2. A device according to claim 1, characterized in that said electrolytic cells are connected in series in such a manner that the cathode space and the anode space are arranged in alternating relationship.
3. A device according to claim 1 - 2, characterized in that the electrolytic cells are pressed together under a prestressing force, whereby the outer shell is connected to the two end plates by being glued, bolted or welded thereto.
4. A cell element according to claim 1, characterized in that the connection between the cathode space and the catholyte space comprises two openings, one opening of which is present in the underside for supplying catholyte, and one opening is present in the upper side for discharging hydrogen gas-containing catholyte.
5. A cell element according to claim 1, characterized in that the connection between the anode space and the anolyte space comprises two openings, of which one opening is present in the underside for supplying anolyte, and one opening is present in the upper side for discharging chlorine gas-containing anolyte.
6. A cell element according to claims 4 - 5, characterized in that the volume of the space for discharging the gas being produced is larger than the volume of the space adjacent to the space that houses the bipolar electrode.

7. A cell element according to claims 4 - 6, characterized in that said cell element provided with a recess, into which the bipolar electrode can be placed, which recess is provided with ridges all round.

8. A cell element according to claims 4 - 7, characterized in that both the anolyte space and the catholyte space have a P-shaped geometry, which P-shaped geometry is determined by an intermediate member, which is connected to the space into which said bipolar electrode is to be placed.

9. A method for carrying out an electrolytic process in an electrolysis device, characterized in that said electrolytic process is carried out in the device according to claims 1 - 3.

10. A method according to claim 9, characterized in that the liquid level of the anolyte in said anolyte space is adjusted such that the chlorine gas formed on the anode is discharged in the form of bubbles by the anolyte liquid.

11. A method according to claim 9, characterized in that the liquid level of the catholyte in said catholyte space is adjusted such that the hydrogen gas formed on the cathode is discharged in the form of bubbles by the catholyte liquid.

12. Use of the chlorine gas obtained in accordance with the method defined in claims 9 - 11 for preparing chlorine dioxide.

13. Use according to claim 12, characterized in that the chlorine gas obtained in accordance with the method defined in claims 9 - 11 is reacted with sodium chlorite.

14. Use according to claims 12 - 13, characterized in that the reaction is carried out at a reduced pressure.

15. Use according to claims 12 - 14, characterized in that said chlorine gas is mixed with an inert carrier gas prior to being reacted with sodium chlorite.

16. Use according to claim 15, characterized in that said inert carrier gas is mixed with said chlorine gas in the anolyte space of the device according to claims 1 - 3.

17. Use according to claims 15 - 16, characterized in that air is used.

18. A reactor for using chlorine gas obtained in accordance with the method defined in claims 9 - 11 for the preparation of chlorine dioxide, characterized in that said reactor is provided with packing

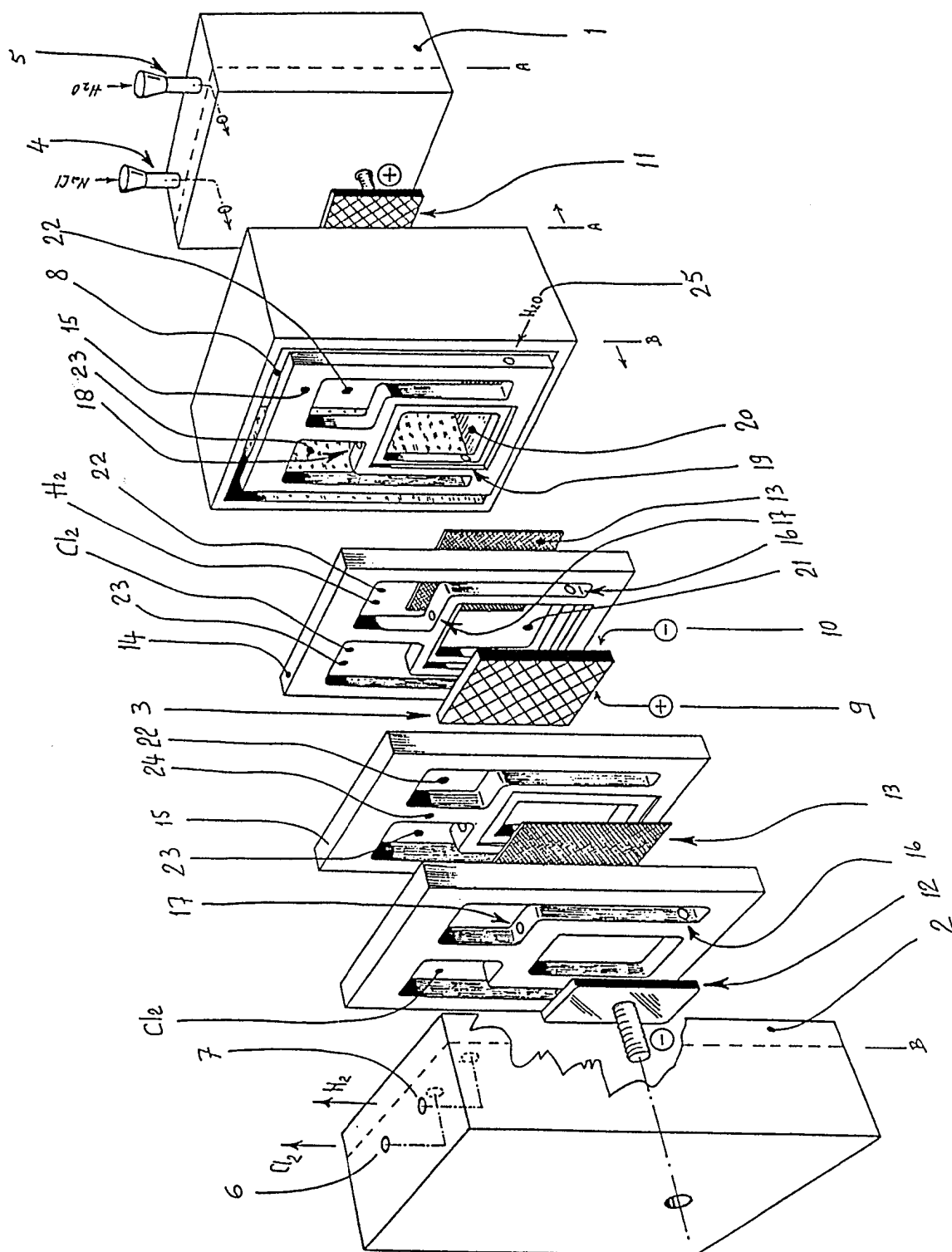
elements.

19. Installation for preparing chlorine dioxide by using chlorine gas obtained in accordance with the method defined in claims 9 - 11, characterized in that said installation comprises the device according to claims 1 - 3 and the reactor according to claim 18.

5

20. Installation according to claim 19, characterized in that said installation comprises a control valve for the delivery of both chlorine gas and chlorine dioxide.

1/1



INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 98/00047

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C25B9/00 C25B1/26 C01B11/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C25B C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 427 340 A (ZILVOLD HYDROTECHNIEK) 15 May 1991 cited in the application see column 5 - column 6; claims 1-8 see figures 1,2	1,2,4-6, 9-11
Y	DE 36 03 254 A (HT-HYDROTECHNIK GMBH) 6 August 1987 cited in the application see column 17, line 31 - column 18, line 21 see figure 11	1,2,4-6, 9-11
A	FR 2 382 519 A (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 29 September 1978 see page 18 - page 21; claims 1-24 see figures 1,2	1
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search

19 March 1998

Date of mailing of the international search report

30/03/1998

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Groseiller, P

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 98/00047

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 11 73 069 B (ELEKTOCHEMISCHE WERKE MÜNCHEN) 2 July 1964 see the whole document ---	12,13, 15,17-19
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 061 (C-567), 10 February 1989 & JP 63 253007 A (OSAKA SODA CO LTD), 20 October 1988, see abstract ---	12,15, 17,19
A	US 4 250 144 A (RATIGAN BRIAN J) 10 February 1981 see column 3, line 28 - line 54 see claims; figure ---	12,18,19
A	CH 671 966 A (MILORAD TOPIC) 13 October 1989 see claims -----	12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 98/00047

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 427340 A	15-05-91	NL 8902713 A DE 69002305 T ES 2044415 T	03-06-91 10-02-94 01-01-94
DE 3603254 A	06-08-87	NONE	
FR 2382519 A	29-09-78	GB 1595193 A AR 214774 A AT 353812 B AU 514448 B AU 3377678 A BE 864363 A BR 7801308 A CA 1107685 A CH 631746 A DD 134123 A DE 2809333 A JP 1308911 C JP 53124198 A JP 60031913 B NL 7802371 A SE 449233 B SE 7802385 A US 4204939 A ZA 7801077 A	12-08-81 31-07-79 10-12-79 12-02-81 06-09-79 28-08-78 26-09-78 25-08-81 31-08-82 07-02-79 07-09-78 26-03-86 30-10-78 25-07-85 06-09-78 13-04-87 05-09-78 27-05-80 31-01-79
DE 1173069 B		NONE	
US 4250144 A	10-02-81	DE 3022273 A FR 2459202 A	18-12-80 09-01-81
CH 671966 A	13-10-89	NONE	